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Spring 2015 Research Report

Synthesis and Self-Assembly of Bottlebrush Block Copolymers

Introduction and Purpose:

When block copolymers are annealed properly they may self-assemble into well-ordered domains of various morphologies based on the volume fraction of each component, the total number of repeat units in the entire polymer and the interaction parameter of the species in the polymer.[1] This results from the immiscibility of the constituents and the chemical bond preventing them from completely separating.[2] Possible morphologies include layers called lamellae, cylinders, and spheres, and depending on the morphology and domain size, a self-assembled block copolymer may have many important applications ranging from photonics, nanotubes, and nanocapsules to filtration and medicine delivery.[1, 2, 3, 4, 5] However, many of these applications require large domain spacings,[1, 2, 5] and traditional linear block copolymers present challenges in achieving domain sizes of greater than 100 nm.[1] This is due to the coiling that occurs in linear polymers. Achieving a domain spacing greater than 100 nm would require linear block copolymers at molecular weights that are difficult to synthesize.[1] Furthermore, due to the entanglements that occur in such large linear polymers, it is difficult to achieve well-ordered domains using them.[1, 5]

One possible solution to this may be to use what are known and bottlebrush block copolymers (Figure 1). Bottlebrush polymers consist of a linear backbone with polymer side chains attached to each repeat unit of the backbone.[1, 4, 5, 6, 7] Due to the steric strain surrounding the backbone, coiling and entanglements do not occur as they would in a linear polymer, causing bottlebrush polymers to behave much more like rigid cylinders.[1, 4, 5, 6, 7] This allows for the formation of much larger domains than in linear block copolymers. There are also more features to be adjusted in bottlebrush block copolymers than in traditional linear block copolymers. Linear block copolymers depend only on the total polymer size and the fraction on each species in the

polymer. Bottlebrush block copolymers depend on the backbone length, total volume fraction of each species, the number of repeat units containing each species, the side chain lengths, the ratios of the side chain lengths of each species relative to each other, and the side chain length relative to the backbone length. The purpose of this research was to better understand the role all of these aspects play in the morphologies and self-assembly of bottlebrush block copolymers.

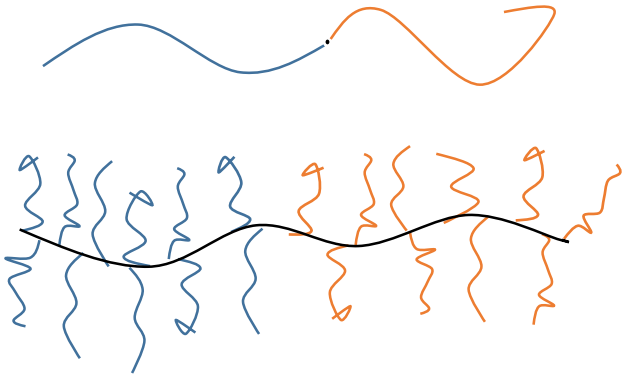

Figure 1. Linear (top) and bottlebrush (bottom) block copolymers.

Methods:

In addition to the bottlebrush block copolymers discussed in the previous report, several more bottlebrush block copolymers were synthesized from existing macromonomer remaining from the previous semester according to the previously reported procedure. The new bottlebrushes were all composed of a roughly 2.0 kg/mol atactic polypropylene-norbornene and 3.8 kg/mol polystyrene-norbornene macromonomer. Molar masses were determined by ^{1}H NMR end group analysis. Once several polymers were synthesized, they were prepared for small-angle X-ray scattering (SAXS) by solvent casting them from a minimal amount of tetrahydrofuran and thermally annealed at 170 °C for 4 hours.

Polymer thin films were also prepared for atomic force microscopy (AFM) analysis (Table 1). Polymer samples were dissolved in toluene at concentrations ranging from 10 to 40 mg/mL and were spin coated at either 3,000 or 10,000 RPM. The resulting thin films were annealed by solvent vapor on a platform in a sealed chamber with either 0.4 or 4.0 mL of toluene in the bottom of the chamber (Figure 2) for times ranging from 30 seconds to 20 minutes if 4.0 mL of solvent was used and 60 to 120 minutes if 0.4 mL of solvent was used. Annealing times were based on the molar mass of the polymer in in the film. The solvent used for spin coating was also the solvent used in annealing. Sample heights were determined by ellipsometry and images were obtained via AFM in peak force mode. Peak force set point, lift height, frequency, and other settings were adjusted as needed to obtain the best image.

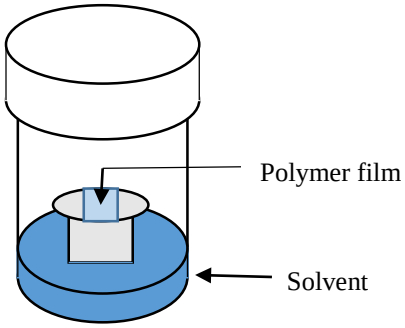

Figure 2. Solvent vapor annealing chamber used for sample preparation.

Table 1. List of polymers imaged by atomic force microscopy.

Entry	M_n (kg/mol)[a]	ϕ_{aPP}[b]	$DP_{aPP\text{-}NB}$	$DP_{PS\text{-}NB}$	$M_{n\ aPP\text{-}NB}$ (kg/mol)[c]	$M_{n\ PS\text{-}NB}$ (kg/mol)[c]
1	28.3	0.51	6.3	3.9	2.1	4.0
2	109.7	0.50	23.9	3.0	2.1	20
3	87.0	0.81	32.7	1.0	2.1	20
4	136.0	0.23	12.8	5.4	2.1	20
5	446.6	0.54	105.8	11.4	2.1	20
6	1,000	0.62	278.1	107.5	2.1	4.0
7	84.0	0.80	32.0	4.4	2.1	3.8
8	95.9	0.43	17.9	15.6	2.1	3.8
9	119.8	0.35	17.9	21.9	2.1	3.8
10	174.5	0.25	17.9	36.4	2.1	3.8
11	328.1	0.13	17.9	76.9	2.1	3.8
12	122.9	0.63	34.7	13.7	2.1	3.8
13	169.4	0.75	58.5	13.0	2.1	3.8
14	256.4	0.84	101.8	12.6	2.1	3.8
15	302.9	0.62	84.3	34.3	2.1	3.8
16	392.2	0.73	131.2	32.5	2.1	3.8
17	497.7	0.79	182.5	32.6	2.1	3.8

[a]Determined by SEC-MALLS. [b]Determined by comparing relative amounts of macromonomers used, taking unreacted macromonomer into consideration, as determined by SEC. [c]Determined by ^{1}H NMR

Results and Discussion:

Two samples were imaged after being cast from and annealed with toluene for various amounts of time, and the images obtained for the samples showed ordering (Figure 3). The image on the left in Figure 3 (entry 7 in Table 1) shows a clear cylindrical morphology with many cylinders aligned perpendicular to the substrate while some remain parallel to it. The image on the right in Figure 3 (entry 5 in Table 1) appears to show cylinders as well that are perpendicular to the substrate. This is an interesting result because of the large molar mass of the polymer (447 kg/mol) and because the polymer was 54% aPP-NB by volume. In this case the majority block formed cylinders. This is likely due to the large disparity in side chain length. This demonstrates the important role that symmetry or asymmetry in the lengths of the side chains has on the

morphology of the thin film. After positive results were obtained for these samples, several more samples were prepared following the same procedure. However, it was found that the majority of samples imaged by this method had either begun to dewet, were still disordered, or one of the blocks was preferentially coating the surface (Figure 4). Experimenting with different annealing times and thermal annealing gave no better images.

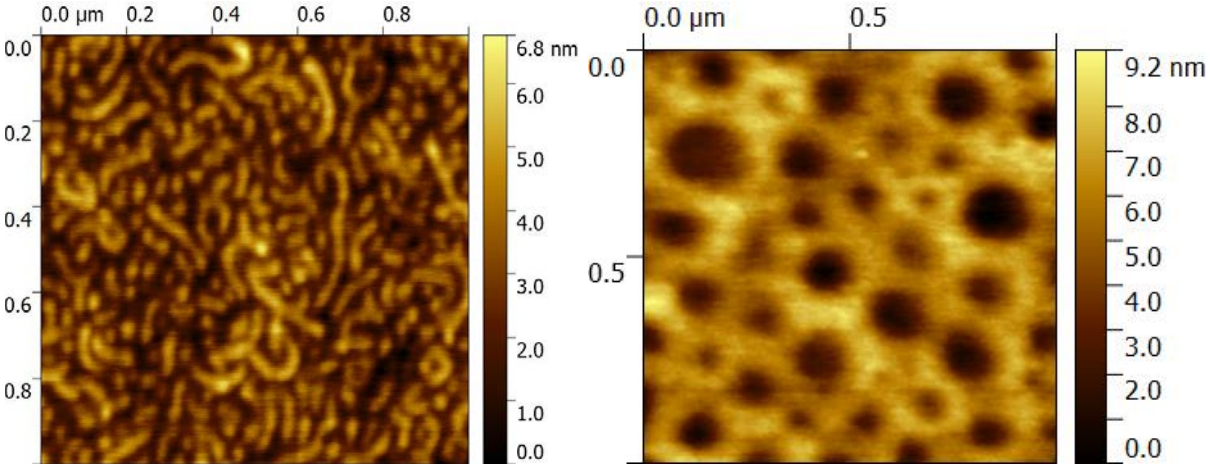

Figure 3. AFM images of entry 7 in Table 1 (left) and entry 5 in Table 1.

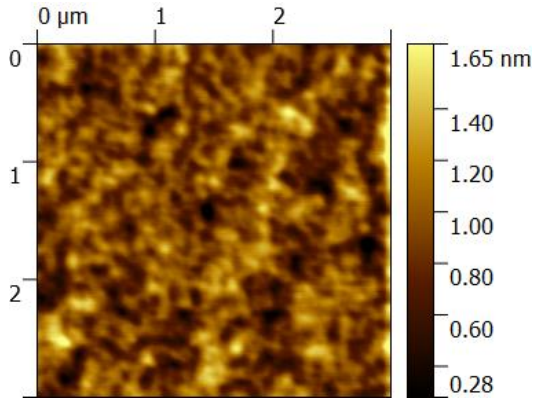

Figure 4. A disordered polymer film that had begun to dewet as evidenced by the large dark spots on the image. Image is of entry 11 in Table 1.

Alternative solvents were sought to see if they might give more ordered samples. The polymer chosen was a highly asymmetric polymer with the majority block being atactic polypropylene (entry 14 in Table 1). Samples were prepared using the same concentrations, spin coating speed, and annealing procedure, yet ellipsometry showed very different sample heights (Table 2). The effect of solvent on sample height will be the focus of further research, both literary and experimental. The images from all of the other solvents turned out to be much more promising as shown in Figure 5. Using tetrahydrofuran gave a branched morphology with the polystyrene block coating the surface. Chloroform appeared to be beginning to form a vertical cylindrical morphology with areas where the polystyrene was still coating the surface. The hexanes and cyclohexane images appeared to show some ordering, but they were not conclusive. Further research will involve using various solvents to find the best one for ordering samples, and collecting AFM images of well-ordered samples from each bottlebrush block copolymer collected.

Table 2. The thickness of the films of a spin coated at 3,000 RPM with the polymer dissolved in various solvents.

Annealing Solvent	Concentration (mg/mL)	Film Thickness (nm)[a]	PS on the surface (%)[b]
Chloroform	20	138	53
Cyclohexane	20	132	24
Hexanes	20	139	16
Tetrahydrofuran	20	118	56
Toluene	20	84	53

[a]Determined by ellipsometry. [b]Determined by particle analysis of adhesion images using ImageJ software. The polymer analyzed was 16% PS-NB by volume (entry 14 on Table 1).

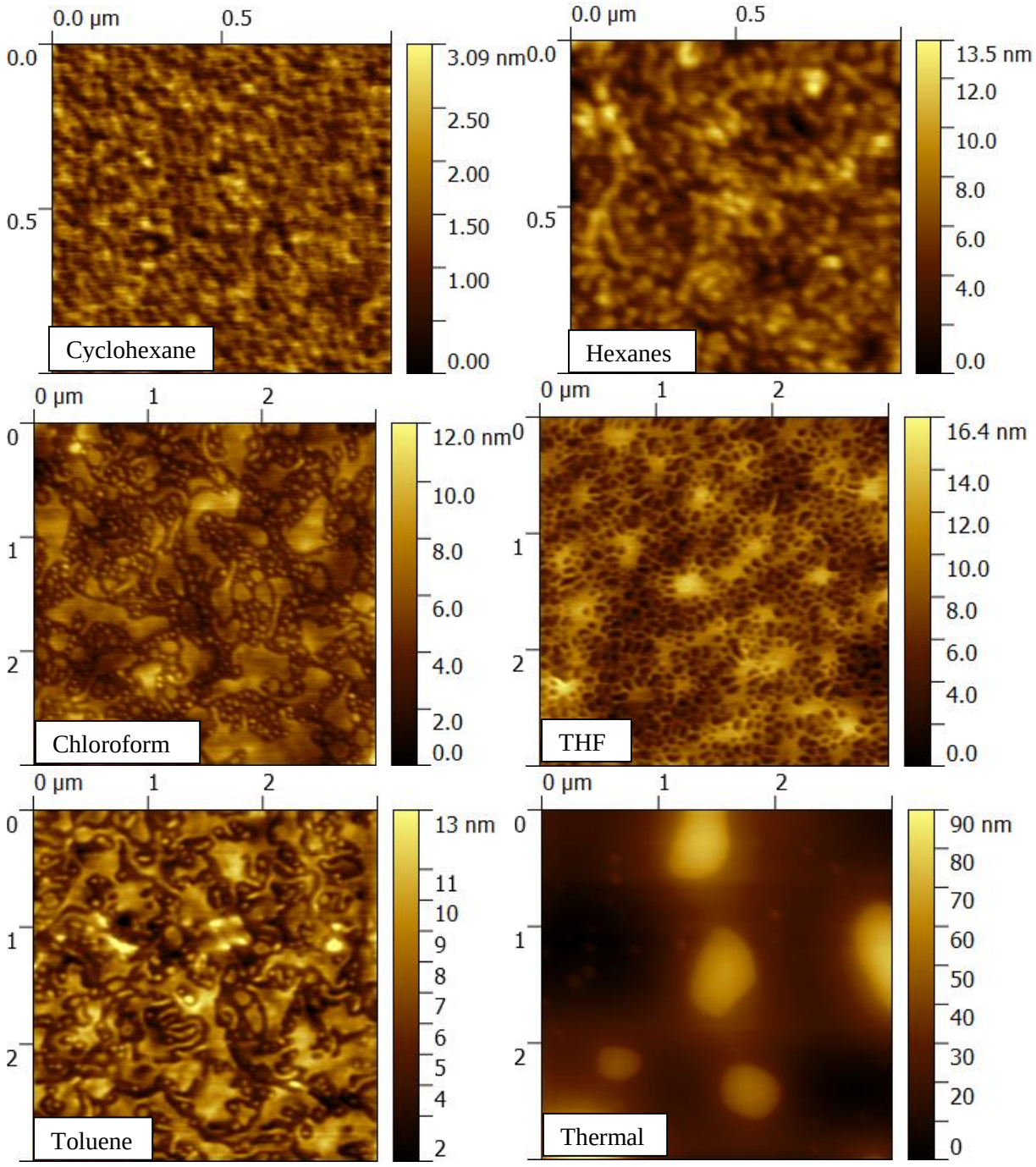

Figure 5. The images of a 254 kg/mol bottlebrush block copolymer composed of aPP-NB and PS-NB that is 84% aPP-NB by volume with 2.1 kg/mol aPP-NB sidechains and 3.8 kg/mol PS-NB side chains (entry 14 on table 1). The samples were spin coated from and annealed using cyclohexane, hexanes, chloroform, tetrahydrofuran, and toluene. Image F was obtained from a sample that was spin coated from toluene and thermally annealed at 110°C for 8 hours. Sample heights correspond to the heights in Table 2.

One success of this project has been the use of the mechanical properties images collected from peak force atomic force microscopy. These images have been used in comparison to their respective height images to determine which block is responsible for features in the height image if it was not immediately obvious. Figure 6 shows an example of a case where lamellae formed parallel to the substrate surface (entry 12 in Table 1). The modulus image was used to determine that despite the changes in height, aPP was covering the entire surface of the image. Because aPP is coating the surface, the step height in the image corresponds to an entire lamellar period. This allowed for a quantitative comparison to the SAXS data which gave a domain spacing of 32nm while the step height in the image was 27±5nm. Future work will involve more quantitative analysis of AFM images like this to serve as a comparison to SAXS data.

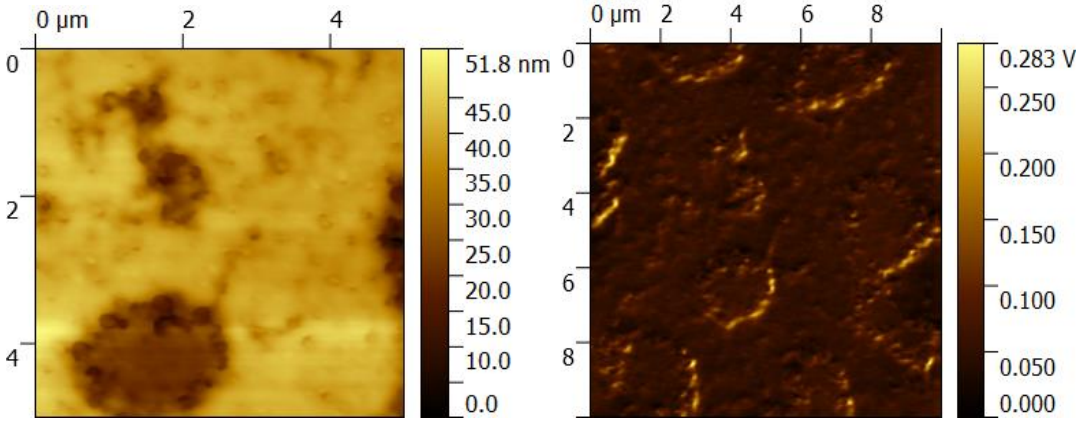

Figure 6. The height (left) and modulus (right) images of a 122 kg/mol bottlebrush block copolymer that is 63% aPP by volume with 2.1 kg/mol aPP-NB branches and 3.8 kg/mol PS-NB branches (entry 12 in Table 1).

Current and Future Research

Current research is focused on characterizing existing bottlebrush block copolymers using AFM, TEM, and SAXS to determine morphology. New sample preparation approaches for AFM, like those previously stated, will be used in an attempt acquire more ordered thin films that will

give higher quality images and will be useful in determining the morphology of polymer samples. More bottlebrush block copolymers will be synthesized adjusting parameters like total molar mass, side chain dimensions, and volume fraction of the constituent polymers. These will also be characterized using SAXS, TEM, and AFM. From these results, the aim is to construct a comprehensive phase diagram for bottlebrush block copolymers taking into account total degree of polymerization of the bottlebrush, percent composition, and side chain dimensions.

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